



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: C11D 11/00, 11/04, 17/06	A1	(11) International Publication Number: WO 99/03964 (43) International Publication Date: 28 January 1999 (28.01.99)
(21) International Application Number: PCT/US98/14056 (22) International Filing Date: 8 July 1998 (08.07.98) (30) Priority Data: 60/052,464 14 July 1997 (14.07.97) US (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): ACHANTA, Srinivas [IN/US]; 707 W. Martin Luther King Drive #607E, Cincinnati, OH 45220 (US). BEIMESCH, Wayne, Edward [US/US]; 711 Red Bud Drive, Covington, KY 41015 (US). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		(81) Designated States: BR, CA, CN, JP, MX, TR, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: PROCESS FOR MAKING A LOW DENSITY DETERGENT COMPOSITION BY CONTROLLED AGGLOMERATION IN A FLUID BED DRYER (57) Abstract A process for producing a low density detergent composition is provided. The process involves: (a) agglomerating a detergent surfactant paste or precursor thereof and dry starting detergent material in a first high speed mixer to obtain detergent agglomerates; (b) mixing the detergent agglomerates in a second high speed mixer to obtain built-up agglomerates; and (c) feeding the built-up agglomerates and a binder into a fluid bed dryer to form detergent agglomerates having a density in a range from about 300 g/l to about 550 g/l, the fluid bed dryer being operated at a Stokes Number of less than about 1, wherein Stokes Number = $8\rho v d/9\mu$, ρ is the apparent particle density of the built-up agglomerates, v is the excess velocity of the built-up agglomerates, d is the mean particle diameter of the built-up agglomerates and μ is the viscosity of the binder.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

**PROCESS FOR MAKING A LOW DENSITY DETERGENT COMPOSITION BY
CONTROLLED AGGLOMERATION IN A FLUID BED DRYER**

5

FIELD OF THE INVENTION

The present invention generally relates to a process for producing a low density detergent composition. More particularly, the invention is directed to a process during which low density detergent agglomerates are produced by feeding a surfactant paste or liquid acid precursor of anionic surfactant and dry starting detergent material sequentially into two high speed mixers followed by a fluid bed dryer in which the agglomeration is controlled to produce the desired low density detergent composition. The low density detergent composition produced by the process can be commercially sold as a conventional non-compact detergent composition or used as an admix in a low dosage, "compact" detergent product.

BACKGROUND OF THE INVENTION

Recently, there has been considerable interest within the detergent industry for laundry detergents which are "compact" and therefore, have low dosage volumes. To facilitate production of these so-called low dosage detergents, many attempts have been made to produce high bulk density detergents, for example with a density of 600 g/l or higher. The low dosage detergents are currently in high demand as they conserve resources and can be sold in small packages which are more convenient for consumers. However, the extent to which modern detergent products need to be "compact" in nature remains unsettled. In fact, many consumers, especially in developing countries, continue to prefer a higher dosage levels in their respective laundering operations. Consequently, there is a need in the art of producing modern detergent compositions for flexibility in the ultimate density of the final composition.

Generally, there are two primary types of processes by which detergent granules or powders can be prepared. The first type of process involves spray-drying an aqueous detergent slurry in a spray-drying tower to produce highly porous detergent granules. In the second type of process, the various detergent components are dry mixed after which they are agglomerated with a binder such as a nonionic or anionic surfactant. In both processes, the most important factors which govern the density of the resulting detergent granules are the density, porosity and surface area, shape of the various starting materials and their respective chemical composition. These parameters, however, can only be varied within a limited range. Thus, flexibility in the substantial bulk density can only be

achieved by additional processing steps which lead to lower density of the detergent granules.

There have been many attempts in the art for providing processes which increase the density of detergent granules or powders. Particular attention has been given to densification of spray-dried granules by post tower treatment. For example, one attempt involves a batch process in which spray-dried or granulated detergent powders containing sodium tripolyphosphate and sodium sulfate are densified and spheronized in a Marumerizer®. This apparatus comprises a substantially horizontal, roughened, rotatable table positioned within and at the base of a substantially vertical, smooth walled cylinder. This process, however, is essentially a batch process and is therefore less suitable for the large scale production of detergent powders. More recently, other attempts have been made to provide continuous processes for increasing the density of "post-tower" or spray dried detergent granules. Typically, such processes require a first apparatus which pulverizes or grinds the granules and a second apparatus which increases the density of the pulverized granules by agglomeration. While these processes achieve the desired increase in density by treating or densifying "post tower" or spray dried granules, they do not provide a process which has the flexibility of providing lower density granules.

Moreover, all of the aforementioned processes are directed primarily for densifying or otherwise processing spray dried granules. Currently, the relative amounts and types of materials subjected to spray drying processes in the production of detergent granules has been limited. For example, it has been difficult to attain high levels of surfactant in the resulting detergent composition, a feature which facilitates production of detergents in a more efficient manner. Thus, it would be desirable to have a process by which detergent compositions can be produced without having the limitations imposed by conventional spray drying techniques.

To that end, the art is also replete with disclosures of processes which entail agglomerating detergent compositions. For example, attempts have been made to agglomerate detergent builders by mixing zeolite and/or layered silicates in a mixer to form free flowing agglomerates. While such attempts suggest that their process can be used to produce detergent agglomerates, they do not provide a mechanism by which conventional starting detergent materials in the form of surfactant pastes or precursors thereof, liquids and dry materials can be effectively agglomerated into crisp, free flowing detergent agglomerates having low densities rather than high densities. In the past, attempts at producing such low density agglomerates involves a nonconventional detergent ingredient which is typically expensive, thereby adding to the cost of the detergent product. One such example of this involves a process of agglomerating with inorganic double salts such as Burkeite to produce the desired low density agglomerates.

Accordingly, there remains a need in the art to have a process for producing a low density detergent composition directly from starting detergent ingredients without the need for relatively expensive specialty ingredients. Also, there remains a need for such a process which is more efficient, flexible and economical to facilitate large-scale production of
5 detergents of low as well as high dosage levels.

BACKGROUND ART

The following references are directed to densifying spray-dried granules: Appel et al, U.S. Patent No. 5,133,924 (Lever); Bortolotti et al, U.S. Patent No. 5,160,657 (Lever); Johnson et al, British patent No. 1,517,713 (Unilever); and Curtis, European Patent
10 Application 451,894. The following references are directed to producing detergents by agglomeration: Beerse et al, U.S. Patent No. 5,108,646 (Procter & Gamble); Capeci et al, U.S. Patent No. 5,366,652 (Procter & Gamble); Hollingsworth et al, European Patent Application 351,937 (Unilever); and Swatling et al, U.S. Patent No. 5,205,958. The following references are directed to inorganic double salts: Evans et al, U.S. Patent No.
15 4,820,441 (Lever); Evans et al, U.S. Patent No. 4,818,424 (Lever); Atkinson et al, U.S. Patent No. 4,900,466 (Lever); France et al, U.S. Patent No. 5,576,285 (Procter & Gamble); and Dhalewadika et al, PCT WO 96/04359 (Unilever).

SUMMARY OF THE INVENTION

The present invention meets the aforementioned needs in the art by providing a
20 process which produces a low density (below about 600 g/l) detergent composition directly from starting ingredients without the need for expensive specialty ingredients such as inorganic double salts. The process does not use the conventional spray drying towers currently used and is therefore more efficient, economical and flexible with regard to the variety of detergent compositions which can be produced in the process. Moreover, the
25 process is more amenable to environmental concerns in that it does not use spray drying towers which typically emit particulates and volatile organic compounds into the atmosphere. The process essentially includes two high speed mixers followed by a fluid bed which is operated such that the Stokes Number for agglomerate coalescence is within a selected range. This results in the formation of the desired low density detergent
30 composition.

As used herein, the term "agglomerates" refers to particles formed by agglomerating detergent granules or particles which typically have a smaller median particle size than the formed agglomerates. As used herein, the phrase "median particle size" means the particle size diameter value above which 50% of the particles have a larger
35 particle size and below which 50% of particles have a smaller particle size. As used herein, "excess velocity" means the amount of velocity of the particles or agglomerates above the minimum fluidization velocity of said particles or agglomerates, wherein the minimum

fluidization velocity is the minimum velocity needed to move said particles which can be calculated, e.g., via the Wen and Yu equation. All percentages used herein are expressed as "percent-by-weight" on an anhydrous basis unless indicated otherwise. All documents cited herein are incorporated herein by reference in their entirety.

5 In accordance with one aspect of the invention, a process for preparing low density detergent agglomerates is provided. The process comprises the steps of: (a) agglomerating a detergent surfactant paste or precursor thereof and dry starting detergent material in a first high speed mixer to obtain agglomerates; (b) mixing the detergent agglomerates in a second high speed mixer to obtain built-up agglomerates; and (c) feeding the built-up agglomerates
10 and a binder into a fluid bed dryer to form said low density detergent agglomerates having a density in a range from about 300 g/l to about 550 g/l, the fluid bed dryer being operated at a Stokes Number of less than about 1, wherein Stokes Number = $8\rho vd/9\mu$, ρ is the apparent particle density of the built-up agglomerates, v is the excess velocity of the built-up agglomerates, d is the mean particle diameter of the built-up agglomerates and μ is the
15 viscosity of the binder.

In accordance with another aspect of the invention, another process for preparing low density detergent agglomerates is provided. The process comprises the steps of: (a) agglomerating a first liquid acid precursor of an anionic surfactant and dry starting detergent material in a first high speed mixer to obtain agglomerates; (b) mixing the
20 detergent agglomerates in a second high speed mixer to obtain built-up agglomerates; (c) adding a second liquid acid precursor of an anionic surfactant to the second high speed mixer; and (d) feeding the built-up agglomerates and a binder into a fluid bed dryer to form low density detergent agglomerates having a density in a range from about 300 g/l to about 550 g/l, the fluid bed dryer being operated at a Stokes Number in a range of from about 0.1
25 to about 0.5, wherein Stokes Number = $8\rho vd/9\mu$, ρ is the apparent particle density of the built-up agglomerates, v is the excess velocity of the built-up agglomerates, d is the mean particle diameter of the built-up agglomerates and μ is the viscosity of the binder. The detergent products made in accordance with any of the process embodiments described herein are also provided.

30 Accordingly, it is an object of the invention to provide a process for producing a low density detergent composition directly from starting detergent ingredients which does not include relatively expensive specialty ingredients. It is also an object of the invention to provide such a process which is more efficient, flexible and economical so as to facilitate large-scale production of detergents of low as well as high dosage levels. These and other
35 objects, features and attendant advantages of the present invention will become apparent to those skilled in the art from a reading of the following detailed description of the preferred embodiment and the appended claims.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention is directed to a process in which low density agglomerates are produced by selectively controlling the operation of the fluid bed dryer in the process as detailed hereinafter. The process forms free flowing, low density detergent agglomerates which can be used alone as the detergent product or as an admixture with conventional spray-dried detergent granules and/or high density detergent agglomerates in a final commercial detergent product. It should be understood that the process described herein can be operated continuously or in a batch mode depending upon the particularly desired application. One major advantage of the present process is that it utilizes equipment which can be operated differently from the present process parameters to obtain high density detergent compositions. In this way, a single large-scale commercial detergent manufacturing facility can be built to produce high or low density detergent compositions depending upon the local consumer demand and its inevitable fluctuations between compact and non-compact detergent products.

Process

In the first step of the process, a detergent surfactant paste or precursor thereof as set forth in more detail hereinafter and dry starting detergent material having a selected median particle size is inputted and agglomerated in a high speed mixer. Unlike previous processes in this area, the dry starting material can include only those relatively inexpensive detergent materials typically used in modern granular detergent products. Such ingredients, include but are not limited to, builders, fillers, dry surfactants, and flow aides. Preferably, the builder includes aluminosilicates, crystalline layered silicates, phosphates, carbonates and mixtures thereof which is the essential dry starting detergent ingredient within the scope of the current process. Relatively expensive materials such as Burkeite ($\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$) and the various silicas are not necessary to achieve the desired low density agglomerates produced by the process. Rather, it has been found that by judiciously controlling particle build-up via process equipment operating parameters, agglomerates having a high degree of "intraparticle" or "intragranule" or "intraagglomerate" porosity, and therefore are low in density, can be produced by the present process. The terms "intraparticle" or "intragranule" or "intraagglomerate" are used synonymously herein to refer to the porosity or void space inside the formed built-up agglomerates produced at any stage of the process. In the first step of the process, the median particle size of the dry detergent material is preferably in a range from about 5 microns to about 70 microns, more preferably from about 10 microns to about 60 microns, and most preferably from about 20 microns to about 50 microns.

The high speed mixer can be any one of a variety of commercially available mixers such as a Lödige CB 30 mixer or similar brand mixer. These types of mixers essentially

consist of a horizontal, hollow static cylinder having a centrally mounted rotating shaft around which several shovel and rod-shaped blades are attached. Preferably, the shaft rotates at a speed of from about 100 rpm to about 2500 rpm, more preferably from about 300 rpm to about 1600 rpm. Preferably, the mean residence time of the detergent ingredients in the high speed mixer is preferably in range from about 2 seconds to about 45 seconds, and most preferably from about 5 seconds to about 15 seconds. This mean residence time is conveniently measured by dividing the weight of the mixer at steady state by throughput (kg/hr) flow. Another suitable mixer is any one of the various Flexomix models available from Schugi (Netherlands) which are vertically positioned high speed mixers. This type of mixer is preferably operated at the same speeds and mean residence times as noted above with respect to the Lödige CB mixers.

In a preferred embodiment of the process invention, a liquid acid precursor of an anionic surfactant is inputted with the dry starting detergent material which at least includes a neutralizing agent such as sodium carbonate. The preferred liquid acid surfactant precursor is C₁₁₋₁₈ linear alkylbenzene sulfonate surfactant ("HLAS"), although any acid precursor of an anionic surfactant may be used in the process. A more preferred embodiment involves feeding a liquid acid precursor of C₁₂₋₁₄ linear alkylbenzene sulfonate surfactant with a C₁₀₋₁₈ alkyl ethoxylated sulfate ("AS") surfactant into the first high speed mixer, preferably in a weight ratio of from about 5:1 to about 1:5, and most preferably, in a range of from about 1:1 to about 3:1 (HLAS:AS). The result of such mixing is a "dry neutralization" reaction between the HLAS and the sodium carbonate embodied in the dry starting detergent material, all of which forms agglomerates.

In the high speed mixers, the detergent agglomerates are formed by building up the particles into low density, light or "fluffy" agglomerated particles having a high degree of intraparticle porosity (i.e., large void spaces inside the built-up agglomerates). The rate of particle size growth can be controlled in a variety of ways, including but not limited to, varying the residence time, temperature and mixing tool speed of the mixer, and controlling amount of liquid or binder inputted into the mixer. In this way, the smaller particle sized starting detergent material is gradually built-up in a controlled fashion such that the agglomerates have a large degree of intraparticle porosity, thereby resulting in a low density detergent. Stated differently, the smaller sized starting detergent material is "glued" or "stuck" together such that there is a large degree of intraparticle porosity.

In the second step of the process, the detergent agglomerates formed in the first step are inputted into a second high speed mixer which can be the same piece of equipment as used in the first step or a different type of high speed mixer. For example, a Lödige CB mixer can be used in the first step while a Schugi mixer is used in the second step. In this process step, the agglomerates having a median particle size as noted previously are mixed

and built-up further in a controlled fashion such that detergent agglomerates having a median particle size of from about 140 microns to about 350 microns, more preferably from about 160 microns to about 220 microns, and most preferably from about 170 microns to about 200 microns. As in the first step of the process, the intraparticle porosity of the particles is increased by "sticking" together smaller sized particles with a high degree of porosity between the starting particles that have been built up. Optionally, a binder can be added to facilitate formation of the desired agglomerates in this step. Typical binders include liquid sodium silicate, a liquid acid precursor of an anionic surfactant such as HLAS, nonionic surfactant, polyethylene glycol or mixtures thereof.

In the next step of the process, the built-up agglomerates (i.e., those agglomerates exiting the second mixer) are inputted into a fluid bed dryer in which the agglomerates are dried and agglomerated to selectively controlled fashion. In this step of the process, the fluid bed dryer is operated at a particle Stokes Number which is less than about 1, more preferably in a range of from about 0.1 to about 0.5, even more preferably from about 0.2 to about 0.4. The particle Stokes Number for agglomerate coalescence is a known parameter for describing the degree of mixing or agglomerating occurring to the particles in a piece of equipment (see Ennis et al, "A microlevel-based characterization of granulation phenomena", *Powder Technology*, 65 (1991)). The Stokes Number = $8\rho v d / 9\mu$, wherein ρ is the apparent particle density of the built-up agglomerates (calculated from the bulk density of the built-up agglomerates assuming an interparticle porosity of 0.4), v is the excess velocity of the built-up agglomerates, d is the mean particle diameter of the built-up agglomerates and μ is the viscosity of the binder. In preferred embodiments of the process invention: ρ is in a range from about 800 g/l to about 1300 g/l, more preferably from about 850 g/l to about 1100 g/l; v is in a range from about 0.1 m/s to about 2 m/s, preferably from about 0.3 m/s to about 1 m/s; d is from about 50 microns to about 2000 microns, preferably from about 100 microns to about 700 microns; and μ is from about 10 cps to about 500 cps, preferably from about 50 cps to about 300 cps.

The density of the agglomerates formed is from about 300 g/l to about 550 g/l, more preferably from about 350 g/l to about 500 g/l, and even more preferably from about 400 g/l to about 480 g/l. All of these densities are generally below that of typical detergent compositions formed of dense agglomerates or most typical spray-dried granules. Preferably, the temperature of the fluid bed dryer is maintained in a range of from about 90°C to about 200°C so as to enhance formation of the desired agglomerates. As with the first and second steps of the process, the agglomerates are built-up from smaller sizes to large sized particles having a high degree of intraparticle porosity. The degree of intraparticle porosity is preferably from about 20% to about 40%, and most preferably from

about 25% to about 35%. The intraparticle porosity can be conveniently measured by standard mercury porosimetry testing.

Preferably, a binder as described previously is added during this step to enhance formation of the desired agglomerates. A particularly preferred binder is liquid sodium silicate. The process may involve adding the binder to both the second high speed mixer as well as the fluid bed dryer, or as stated previously, any one of these locations. It has also been found beneficial to add the binder simultaneously at more than one location in one or more of the steps of the process. For example, the liquid silicate can be added at two locations in the fluid bed dryer, e.g., at or near the inlet port and at or near the exit port. Also, the median binder droplet diameter is from about 20 microns to about 150 microns, a parameter which enhances formation of the desired built-up agglomerates. Further in this regard, the ratio of the median binder droplet diameter to built-up agglomerate (exiting the second high speed mixer) particle diameter is preferably from about 0.1 to about 0.6.

Other optional steps contemplated by the present process include screening the oversized detergent agglomerates in a screening apparatus which can take a variety of forms including but not limited to conventional screens chosen for the desired particle size of the finished detergent product. Other optional steps include conditioning of the detergent agglomerates by subjecting the agglomerates to additional drying and/or cooling by way of apparatus discussed previously.

Another optional step of the instant process entails finishing the resulting detergent agglomerates by a variety of processes including spraying and/or admixing other conventional detergent ingredients. For example, the finishing step encompasses spraying perfumes, brighteners and enzymes onto the finished agglomerates to provide a more complete detergent composition. Such techniques and ingredients are well known in the art.

Detergent Surfactant Paste or Precursor

The liquid acid precursor of anionic surfactant is used in the first step of the process, and in optional embodiments, as a liquid binder in the second and/or third essential steps of the process. This liquid acid precursor will typically have a viscosity measured at 30°C of from about 500 cps to about 5,000 cps. The liquid acid is a precursor for the anionic surfactants described in more detail hereinafter. A detergent surfactant paste can also be used in the process and is preferably in the form of an aqueous viscous paste, although other forms are also contemplated by the invention. This so-called viscous surfactant paste has a viscosity of from about 5,000 cps to about 100,000 cps, more preferably from about 10,000 cps to about 80,000 cps, and contains at least about 10% water, more preferably at least about 20% water. The viscosity is measured at 70°C and at shear rates of about 10 to 100 sec.⁻¹. Furthermore, the surfactant paste, if used, preferably

comprises a deterative surfactant in the amounts specified previously and the balance water and other conventional detergent ingredients.

The surfactant itself, in the viscous surfactant paste, is preferably selected from anionic, nonionic, zwitterionic, ampholytic and cationic classes and compatible mixtures thereof. Detergent surfactants useful herein are described in U.S. Patent 3,664,961, Norris, issued May 23, 1972, and in U.S. Patent 3,919,678, Laughlin et al., issued December 30, 1975, both of which are incorporated herein by reference. Useful cationic surfactants also include those described in U.S. Patent 4,222,905, Cockrell, issued September 16, 1980, and in U.S. Patent 4,239,659, Murphy, issued December 16, 1980, both of which are also incorporated herein by reference. Of the surfactants, anionics and nonionics are preferred and anionics are most preferred.

Nonlimiting examples of the preferred anionic surfactants useful in the surfactant paste, or from which the liquid acid precursor described herein derives, include the conventional C₁₁-C₁₈ alkyl benzene sulfonates ("LAS"), primary, branched-chain and random C₁₀-C₂₀ alkyl sulfates ("AS"), the C₁₀-C₁₈ secondary (2,3) alkyl sulfates of the formula CH₃(CH₂)_x(CHOSO₃⁻M⁺)CH₃ and CH₃(CH₂)_y(CHOSO₃⁻M⁺)CH₂CH₃ where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a

water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, and the C₁₀-C₁₈ alkyl alkoxy sulfates ("AE_xS"; especially EO 1-7 ethoxy sulfates).

Optionally, other exemplary surfactants useful in the paste of the invention include and C₁₀-C₁₈ alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C₁₀-C₁₈ glycerol ethers, the C₁₀-C₁₈ alkyl polyglycosides and their corresponding sulfated polyglycosides, and C₁₂-C₁₈ alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C₁₂-C₁₈ alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C₆-C₁₂ alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), C₁₂-C₁₈ betaines and sulfobetaines ("sultaines"), C₁₀-C₁₈ amine oxides, and the like, can also be included in the overall compositions. The C₁₀-C₁₈ N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C₁₂-C₁₈ N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C₁₂-C₁₈ glucamides can be used for low sudsing. C₁₀-C₂₀ conventional soaps may also be used. If high sudsing is desired, the branched-chain C₁₀-C₁₆ soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts.

Dry Detergent Material

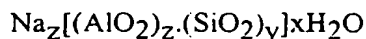
The starting dry detergent material of the present process preferably comprises a builder and other standard detergent ingredients such as sodium carbonate, especially when a liquid acid precursor of a surfactant is used as it is needed as a neutralizing agent in the first step of the process. Thus, preferable starting dry detergent material includes sodium carbonate and a phosphate or an aluminosilicate builder which is referenced as an aluminosilicate ion exchange material. A preferred builder is selected from the group consisting of aluminosilicates, crystalline layered silicates, phosphates, carbonates and mixtures thereof. Preferred phosphate builders include sodium tripolyphosphate, tetrasodium pyrophosphate and mixtures thereof. Additional specific examples of inorganic phosphate builders are sodium and potassium tripolyphosphate, pyrophosphate, polymeric metaphosphate having a degree of polymerization of from about 6 to 21, and orthophosphates. Examples of polyphosphonate builders are the sodium and potassium salts of ethylene diphosphonic acid, the sodium and potassium salts of ethane 1-hydroxy-1, 1-diphosphonic acid and the sodium and potassium salts of ethane, 1,1,2-triphosphonic acid. Other phosphorus builder compounds are disclosed in U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,422,137; 3,400,176 and 3,400,148, all of which are incorporated herein by reference.

The aluminosilicate ion exchange materials used herein as a detergent builder preferably have both a high calcium ion exchange capacity and a high exchange rate. Without intending to be limited by theory, it is believed that such high calcium ion exchange rate and capacity are a function of several interrelated factors which derive from the method by which the aluminosilicate ion exchange material is produced. In that regard, the aluminosilicate ion exchange materials used herein are preferably produced in accordance with Corkill et al, U.S. Patent No. 4,605,509 (Procter & Gamble), the disclosure of which is incorporated herein by reference.

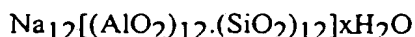
Preferably, the aluminosilicate ion exchange material is in "sodium" form since the potassium and hydrogen forms of the instant aluminosilicate do not exhibit the as high of an exchange rate and capacity as provided by the sodium form. Additionally, the aluminosilicate ion exchange material preferably is in over dried form so as to facilitate production of crisp detergent agglomerates as described herein. The aluminosilicate ion exchange materials used herein preferably have particle size diameters which optimize their effectiveness as detergent builders. The term "particle size diameter" as used herein represents the average particle size diameter of a given aluminosilicate ion exchange material as determined by conventional analytical techniques, such as microscopic determination and scanning electron microscope (SEM). The preferred particle size diameter of the aluminosilicate is from about 0.1 micron to about 10 microns, more

preferably from about 0.5 microns to about 9 microns. Most preferably, the particle size diameter is from about 1 microns to about 8 microns.

Preferably, the aluminosilicate ion exchange material has the formula



- 5 wherein z and y are integers of at least 6, the molar ratio of z to y is from about 1 to about 5 and x is from about 10 to about 264. More preferably, the aluminosilicate has the formula



- wherein x is from about 20 to about 30, preferably about 27. These preferred
10 aluminosilicates are available commercially, for example under designations Zeolite A, Zeolite B and Zeolite X. Alternatively, naturally-occurring or synthetically derived aluminosilicate ion exchange materials suitable for use herein can be made as described in Krummel et al, U.S. Patent No. 3,985,669, the disclosure of which is incorporated herein by reference.

- 15 The aluminosilicates used herein are further characterized by their ion exchange capacity which is at least about 200 mg equivalent of CaCO_3 hardness/gram, calculated on an anhydrous basis, and which is preferably in a range from about 300 to 352 mg equivalent of CaCO_3 hardness/gram. Additionally, the instant aluminosilicate ion exchange materials are still further characterized by their calcium ion exchange rate which
20 is at least about 2 grains Ca^{++} /gallon/minute/-gram/gallon, and more preferably in a range from about 2 grains Ca^{++} /gallon/minute/-gram/gallon to about 6 grains Ca^{++} /gallon/minute/-gram/gallon.

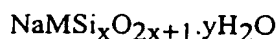
Adjunct Detergent Ingredients

- The starting dry detergent material in the present process can include additional
25 detergent ingredients and/or, any number of additional ingredients can be incorporated in the detergent composition during subsequent steps of the present process. These adjunct ingredients include other detergency builders, bleaches, bleach activators, suds boosters or suds suppressors, anti-tarnish and anticorrosion agents, soil suspending agents, soil release agents, germicides, pH adjusting agents, non-builder alkalinity sources, chelating agents,
30 smectite clays, enzymes, enzyme-stabilizing agents and perfumes. See U.S. Patent 3,936,537, issued February 3, 1976 to Baskerville, Jr. et al., incorporated herein by reference.

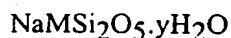
- Other builders can be generally selected from the various borates, polyhydroxy sulfonates, polyacetates, carboxylates, citrates, tartrate mono- and di-succinates, and
35 mixtures thereof. Preferred are the alkali metal, especially sodium, salts of the above. In comparison with amorphous sodium silicates, crystalline layered sodium silicates exhibit a clearly increased calcium and magnesium ion exchange capacity. In addition, the layered

sodium silicates prefer magnesium ions over calcium ions, a feature necessary to insure that substantially all of the "hardness" is removed from the wash water. These crystalline layered sodium silicates, however, are generally more expensive than amorphous silicates as well as other builders. Accordingly, in order to provide an economically feasible laundry detergent, the proportion of crystalline layered sodium silicates used must be determined judiciously.

The crystalline layered sodium silicates suitable for use herein preferably have the formula



wherein M is sodium or hydrogen, x is from about 1.9 to about 4 and y is from about 0 to about 20. More preferably, the crystalline layered sodium silicate has the formula



wherein M is sodium or hydrogen, and y is from about 0 to about 20. These and other crystalline layered sodium silicates are discussed in Corkill et al, U.S. Patent No.

4,605,509, previously incorporated herein by reference.

Examples of nonphosphorus, inorganic builders are tetraborate decahydrate and silicates having a weight ratio of SiO_2 to alkali metal oxide of from about 0.5 to about 4.0, preferably from about 1.0 to about 2.4. Water-soluble, nonphosphorus organic builders useful herein include the various alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates and polyhydroxy sulfonates. Examples of polyacetate and polycarboxylate builders are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylene diamine tetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid.

Polymeric polycarboxylate builders are set forth in U.S. Patent 3,308,067, Diehl, issued March 7, 1967, the disclosure of which is incorporated herein by reference. Such materials include the water-soluble salts of homo- and copolymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid and methylene malonic acid. Some of these materials are useful as the water-soluble anionic polymer as hereinafter described, but only if in intimate admixture with the non-soap anionic surfactant.

Other suitable polycarboxylates for use herein are the polyacetal carboxylates described in U.S. Patent 4,144,226, issued March 13, 1979 to Crutchfield et al, and U.S. Patent 4,246,495, issued March 27, 1979 to Crutchfield et al, both of which are incorporated herein by reference. These polyacetal carboxylates can be prepared by bringing together under polymerization conditions an ester of glyoxylic acid and a polymerization initiator. The resulting polyacetal carboxylate ester is then attached to chemically stable end groups to stabilize the polyacetal carboxylate against rapid

depolymerization in alkaline solution, converted to the corresponding salt, and added to a detergent composition. Particularly preferred polycarboxylate builders are the ether carboxylate builder compositions comprising a combination of tartrate monosuccinate and tartrate disuccinate described in U.S. Patent 4,663,071, Bush et al., issued May 5, 1987, the disclosure of which is incorporated herein by reference.

Bleaching agents and activators are described in U.S. Patent 4,412,934, Chung et al., issued November 1, 1983, and in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, both of which are incorporated herein by reference. Chelating agents are also described in U.S. Patent 4,663,071, Bush et al., from Column 17, line 54 through Column 18, line 68, incorporated herein by reference. Suds modifiers are also optional ingredients and are described in U.S. Patents 3,933,672, issued January 20, 1976 to Bartoletta et al., and 4,136,045, issued January 23, 1979 to Gault et al., both incorporated herein by reference.

Suitable smectite clays for use herein are described in U.S. Patent 4,762,645, Tucker et al, issued August 9, 1988, Column 6, line 3 through Column 7, line 24, incorporated herein by reference. Suitable additional detergency builders for use herein are enumerated in the Baskerville patent, Column 13, line 54 through Column 16, line 16, and in U.S. Patent 4,663,071, Bush et al, issued May 5, 1987, both incorporated herein by reference.

In order to make the present invention more readily understood, reference is made to the following example, which is intended to be illustrative only and not intended to be limiting in scope.

EXAMPLE

This Example illustrates the process invention in which a low density agglomerated detergent composition is prepared. A Lödige CB 30 high speed mixer is charged with a mixture of powders, namely sodium carbonate (median particle size 15 microns) and sodium tripolyphosphate ("STPP") with a median particle size of 25 microns. A liquid acid precursor of sodium alkylbenzene sulfonate surfactant ($C_{12}H_{25}-C_6H_4-SO_3-H$ or "HLAS" as noted below) and a 70% active aqueous C_{10-18} alkyl ethoxylated sulfate surfactant (EO = 3, "AES") paste are also inputted into the Lödige CB 30 mixer, wherein the HLAS is added first. The mixer is operated at 1600 rpm and the sodium carbonate, STPP, HLAS and AES are formed into agglomerates having a median particle size of about 110 microns after a mean residence time in the Lödige CB 30 mixer of about 5 seconds. The agglomerates are then fed to a Schugi (Model # FX160) high speed mixer which is operated at 2800 rpms with a mean residence time of about 2 seconds. A HLAS binder is inputted into the Schugi (Model # FX160) mixer during this step which results in built-up agglomerates having a median particle size of about 180 microns being formed.

Thereafter, the built-up agglomerates are passed through a fluid bed dryer which is operated at a Stokes number of 0.29, wherein ρ is 1035 g/l (apparent particle density of built-up agglomerates exiting the Schugi mixer), v is 0.44 m/s (excess velocity of built-up agglomerates entering the fluid bed assuming a minimum fluidization velocity of 0.3 m/s), d is 178 microns (mean particle diameter of the built-up agglomerates entering the fluid bed) and μ is the sodium silicate binder viscosity of 250 cps. The median droplet diameter of the sodium silicate binder is 40 microns as measured by a Malvern Particle Size Analyzer. The fluid bed inlet air temperature is maintained at about 125°C. At each end of the fluid bed dryer, liquid sodium silicate binder is fed into the fluid bed dryer resulting in the finished detergent agglomerates having a density of about 485 g/l and a median particle size of about 360 microns. Unexpectedly, the finished agglomerates have excellent physical properties in that they are free flowing as exhibited by their superior cake strength grades.

The composition of the agglomerates are given below in Table I.

TABLE I
(% weight)

Component	I
LAS (Na)	15.8
AES (EO = 3)	4.7
Sodium carbonate	48.0
STPP	22.7
Sodium Silicate	5.5
Water	<u>3.3</u>
	100.0

The agglomerates embody about 14% of fines (less than 150 microns) which are recycled from the fluid bed back into the Lödige CB 30 which enhances production of the agglomerates produced by the process.

Having thus described the invention in detail, it will be clear to those skilled in the art that various changes may be made without departing from the scope of the invention and the invention is not to be considered limited to what is described in the specification.

WHAT IS CLAIMED IS:

1. A process for preparing a low density detergent composition characterized by the steps of:

- (a) agglomerating a detergent surfactant paste or precursor thereof and dry starting detergent material in a first high speed mixer to obtain agglomerates;
- (b) mixing said detergent agglomerates in a second high speed mixer to obtain built-up agglomerates; and
- (c) feeding said built-up agglomerates and a binder into a fluid bed dryer to form low density detergent agglomerates having a density in a range from about 300 g/l to about 550 g/l, said fluid bed dryer being operated at a Stokes Number of less than 1, wherein

$$\text{Stokes Number} = 8\rho vd/9\mu$$

ρ is the apparent particle density of said built-up agglomerates, v is the excess velocity of said built-up agglomerates, d is the mean particle diameter of said built-up agglomerates and μ is the viscosity of said binder.

- 2. The process of claim 1 wherein said Stokes Number is in a range from 0.1 to 0.5.
- 3. The process of claim 1 wherein said binder has a median droplet diameter of from 20 microns to 100 microns.
- 4. The process of claim 1 further comprising the step of adding a second binder to said high speed mixer in said step (b).
- 5. The process of claim 1 wherein said binder is sodium silicate.
- 6. The process of claim 1 wherein said Stokes Number is in a range of from 0.1 to 0.5, said ρ is in a range of from 800 g/l to 1400 g/l, said v is in a range from 0.1 m/s to 5m/s, said d is in a range from 50 microns to 2000 microns, and said μ is in a range from 10 cps to about 500 cps.

7. The process of claim 1 wherein said step (a) includes agglomerating a liquid acid precursor of C₁₁₋₁₈ linear alkylbenzene sulfonate surfactant and a C₁₀₋₁₈ alkyl ethoxylated sulfate surfactant.
8. The process of claim 1 wherein said step (c) includes maintaining the temperature of said fluid bed dryer to be in a range of from 90°C to 200°C.
9. The process of claim 1 wherein said dry starting material comprises a builder selected from the group consisting of aluminosilicates, crystalline layered silicates, phosphates, carbonates and mixtures thereof.
10. A detergent composition made in accordance with the process of claim 1.

INTERNATIONAL SEARCH REPORT

Int. l. Application No

PCT/US 98/14056

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D11/00 C11D11/04 C11D17/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 576 285 A (FRANCE PAUL A ET AL) 19 November 1996 cited in the application see column 4, line 15 - column 5, line 10; claims; examples 1,2 ---	1,7-10
A	WO 97 22685 A (UNILEVER) 26 June 1997 see claims; examples 1-7 ---	1,7-10
A	WO 97 12956 A (PROCTER & GAMBLE) 10 April 1997 see claims 1,2; example 1 ---	1,9,10
A	WO 96 04359 A (UNILEVER) 8 February 1996 cited in the application see claims; examples ---	1,7-10
-/--		



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

6 October 1998

Date of mailing of the international search report

22/10/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Grittern, A

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/14056

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, A	WO 97 30145 A (PROCTER & GAMBLE) 21 August 1997 see claims; examples A, B -----	1, 7-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/14056

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 5576285	A	19-11-1996	EP 0858500 A		19-08-1998
			WO 9712955 A		10-04-1997
WO 9722685	A	26-06-1997	AU 1301397 A		14-07-1997
WO 9712956	A	10-04-1997	US 5665691 A		09-09-1997
			AU 7250396 A		28-04-1997
WO 9604359	A	15-02-1996	AU 3165695 A		04-03-1996
			BR 9508505 A		26-05-1998
			CA 2195313 A		15-02-1996
			CZ 9700305 A		17-09-1997
			EP 0775193 A		28-05-1997
			HU 77715 A		28-07-1998
			PL 318548 A		23-06-1997
			SK 14597 A		09-07-1997
WO 9730145	A	21-08-1997	US 5668099 A		16-09-1997

THIS PAGE BLANK (USPTO)